

**STUDIES ON THE FORMULATION AND
MECHANICAL AND DYNAMIC PROPERTIES OF
NATURAL RUBBER/CHLOROPRENE RUBBER
BLEND FOR RUBBER BUSHING APPLICATION**

by

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
λ	Second lame constant
A	Cross sectional area
a_0	Original cross sectional area
BR	Butadiene Rubber
CBS	Cyclohexyl-2-benzothiazyl sulphenamide
CR	Chloroprene Rubber
D	Damping
DCSBR	Dichlorocarbene modified styrene-butadiene rubber
DIN	German Industry Standard
E	Young modulus
e	Deformation
E^*	Complex modulus
E'	Storage modulus
E''	Loss modulus
E_∞	Compression modulus
EB	Elongation at break
E_c	Effective compression modulus
ϵ_i	Principle strain
ENR	Epoxidized Natural Rubber
EPDM	Ethylene Propylene Diene Monomers
ETU	Ethylene Thiourea
f	Disturbing frequency

F	Force
FEF	Fast Extruding Furnace
f_n	Natural frequency
G	First lame constant is equal to the shear modulus
G*	Modulus
G'	In-phase storage modulus
G''	Out-of-phase loss modulus
G_{app}	Apparent shear modulus
G_{eff}	Effective shear modulus
h	Thickness
HAF	High Abrasion Furnace
I	Moment of inertia
IPPD	N- isopropyl N- phenyl – p- phenylenediamine
IR	Isoprene Rubber
IRHD	International Rubber Hardness Degree
ISO	International Organization for Standardization
K	Bulk modulus
K_a	Axial stiffness
K_{app}	Apparent cure rate
K_c	Effective compression stiffness
K_r	Radial stiffness
K_s	Shear stiffness
L	Length
l_o	Original length
M	Mounted mass

M100	Stress at 100% elongation
M300	Stress at 300% elongation
MBS	2 – (Morpholinothio) benzothiazole sulfenamide
NBR	Nitrile Butadiene Rubber
NR	Natural Rubber
NR/CR	Natural Rubber to Chloroprene Rubber blend ratio
ODIP	N, N' – diisopropylthiuram disulphide
Pphr	Part per hundred parts of rubber
PVC	Polyvinyl Chloride
R	Radius
r	Distance
S	Shape factor
S.G	Specific gravity
SBR	Styrene Butadiene rubber
Semi-EV	Semi efficient vulcanization
SMR	Standard Malaysian Rubber
T	Transmissibility
t35	Time required to achieve 35 Mooney units above the minimum viscosity
t5	Time required to achieve 5 Mooney units above the minimum viscosity
T90	Cure time (time required for the storage torque curve to reach 90% of maximum – minimum torque.
T95	Cure time (time required for the storage torque curve to reach 95% of maximum – minimum torque.
TDQ	2,2,4 – Trimethyl-1,2-dihydroquinoline
Tmax	Maximum torque

T_{\min}	Minimum torque
IMTD	Tetramethylthiuram disulphide
TS	Tensile strength
TS2	Scorch time (time required for the storage torque curve to reach 2% of maximum – minimum torque.
U_r	Radial displacement
U_0	Tangential displacement
U_ϕ	Azimuthal displacement
V_r	Volume fraction of rubber
W	Strain energy
x	Static deflection
ZnO	Zinc Oxide
β	Numerical factor
γ_0	Strain of amplitude
δ	Loss angle
ϵ	Strain
η	Isolating efficiency
θ	Tangential
λ	Frequency ratio
λ	Extension ratio
σ	Stress
σ_i	Principle stress
τ_0	Stress of amplitude
ϕ	Azimuthal
ω	Angular frequency (2π times the frequency of oscillation)

KAJIAN KE ATAS FORMULASI DAN SIFAT-SIFAT MEKANIK DAN DINAMIK BAGI ADUNAN GETAH ASLI/GETAH KLOROPRENA UNTUK APLIKASI BUSH GETAH

ABSTRAK

Suatu kajian sistematik, berasaskan formulasi-formulasi adunan getah asli dan getah kloroprena (NR/CR), telah dijalankan untuk mendapatkan satu formulasi yang sesuai untuk bush getah. Kedua-dua sifat-sifat statik dan dinamik telah diambilkira. Sifat-sifat penting yang diambilkira untuk aplikasi bush getah ialah set mampatan yang baik, rintangan penuaan yang baik, dan pemencilan getaran yang baik dengan transmisibiliti yang rendah. Sebatian permulaan yang digunakan adalah satu formulasi 100% getah asli biasa yang digunakan untuk gelas getaran.

Berdasarkan Formulasi 1, kajian ke atas sebatian dan vulkanisat gam 100% NR, 100% CR dan adunan NR/CR pada nisbah 65/35, 70/30, 75/25, 80/20 dan 85/15 telah dijalankan. Kadar pematangan bagi 100%CR didapati perlahan berbanding dengan 100%NR, dan mempamerkan kekerasan, kekuatan tensil yang rendah dan set mampatan yang tinggi. Ciri-ciri pematangan yang lebih baik telah diperhatikan pada adunan NR/CR dan amaun NR yang tinggi memberikan resilien, kekuatan tensil, M300 dan set mampatan yang lebih baik.

Sebatian berpengisi dan vulkanisat berpengisi 100% NR, 100% CR dan adunan NR/CR telah dikaji berdasarkan Formulasi 2 iaitu dengan penambahan 40 bsg pengisi hitam karbon dan 5 bsg minyak pemprosesan ke dalam Formulasi 1. Penambahan hitam karbon mengurangkan masa pemvulkanan dan peningkatan amaun NR meningkatkan

kekuatan tensil dan modulus 300 manakala set mampatan dan rintangan penuaan adalah lebih baik dengan amaun CR yang lebih tinggi. Berdasarkan kepada sifat-sifat keseluruhan kekuatan tensil, resilien, set mampatan dan rintangan penuaan, adunan NR/CR pada nisbah 75/25 telah dipilih untuk kajian seterusnya dengan mempelbagaikan beban hitam karbon pada 0, 10, 20, 30, 40, 50, 60, 70 dan 80 bsg. Peningkatan amaun karbon meningkatkan keeffisienan pemvulkanan dan kekerasan, dan menurunkan resilien dan pemanjangan pada takat putus. Kekuatan tensil melepasi takat maksimum yang nyata dengan peningkatan beban hitam karbon dan mencapai takat optima pada 40 bsg hitam karbon.

Formulasi 3 telah dihasilkan daripada Formulasi 2, dengan kehadiran pencepat istimewa Rhenogran ETU-80. Amaun hitam karbon telah ditingkatkan di dalam Formulasi 3 berbanding dengan Formulasi 2 dengan sewajarnya dan kekerasan yang dikehendaki pada 50, 60, 70 dan 80 Shore A dicapai dengan menambahkan minyak. Kekuatan tensil, pemanjangan pada takat putus, histerisis, set mampatan dan rintangan penuaan yang lebih baik telah diperolehi dengan Formulasi 3 berbanding dengan Formulasi 2 disebabkan oleh kehadiran ETU yang memberikan lebih rangkaian yang kekal semasa pemvulkanan.

Bush-bush getah telah dibuat berdasarkan Formulasi 2 dan Formulasi 3 pada kekerasan 70 Shore A, dan sifat-sifat statik dan dinamik telah ditentukan. Ujian mampatan axial dan radial menunjukkan bahawa bush berdasarkan Formulasi 3 memerlukan daya yang lebih pada canggaan yang tinggi dan memberikan ikatan getah kepada logam yang lebih baik daripada Formulasi 2. Ujian dinamik telah dijalankan pada arah radial 10 000 putaran. Keputusan menunjukkan bahawa bush berdasarkan

Formulasi 3 memberikan derajat pemencilan yang tinggi dan transmisibiliti yang lebih rendah (pemindahan getaran yang lebih rendah)berbanding dengan Formulasi 2.

Boleh disimpulkan bahawa satu formulasi yang sesuai telah berjaya dihasilkan untuk gelas bush yang memberikan keseimbangan yang baik secara keseluruhan dari segi sifat-sifat mekanik, set mampatan, dan rintangan penuaan dengan ciri-ciri pemencilan dan transmisibiliti yang baik.

STUDIES ON THE FORMULATION AND MECHANICAL AND DYNAMIC PROPERTIES OF NATURAL RUBBER/ CHLOROPRENE RUBBER BLEND FOR RUBBER BUSHING APPLICATION

ABSTRACT

A systematic investigation, based on natural rubber and chloroprene rubber (NR/CR) blend formulations, were carried out to develop a suitable formulation for rubber bushing. Both static properties and dynamic properties were considered. The important properties considered for rubber bushing application were good compression set, good ageing resistance and good vibration isolation with low transmissibility. The starting and reference compound used is a typical 100% NR formulation used for vibration mounting.

Based on Formulation 1, the investigation of gum vulcanizates of 100% NR, 100% CR and NR/CR blends of 65/35, 70/30, 75/25, 80/20 and 85/15 by ratio were carried out. The cure rate of 100%CR is slower than 100% NR and displays low hardness, tensile strength and high compression set. Better cure characteristic was observed for the NR/CR blends and higher amount of NR gives better resilience, tensile strength, M300 and compression set.

Filled vulcanizates of 100% NR, 100% CR and NR/CR blends were investigated based on Formulation 2 i.e. by adding 40 phr of carbon black filler and 5 phr of processing oil into Formulation 1. Addition of filler reduces the vulcanization time and higher amount of NR increases the tensile strength and modulus 300 while the

compression set and ageing resistance are better with higher amount of CR. Based on the overall properties of tensile strength, resilience, compression set and ageing resistance, the blend of NR/CR at 75/25 ratio was chosen for a subsequent study by varying the carbon black loading at 0, 10, 20, 30, 40, 50, 60, 70 and 80 phr. Increased in amount of carbon black increases the efficiency of vulcanization and hardness, and decreases the resilience and elongation at break. Tensile strength value passes through a definite maximum with the increased in carbon black loading and the optimum was achieved at 40 phr of carbon black.

Formulation 3 was developed from Formulation 2, with the presence of special accelerator Rhenogran ETU-80. The amount of carbon black was increased in Formulation 3 compared to Formulation 2 accordingly and the required hardness of 50, 60, 70 and 80 Shore A were achieved by adding processing oil. Better tensile strength, elongation at break, hysteresis, compression set and ageing resistance were obtained with Formulation 3 compared to Formulation 2 due to presence of ETU which gives more permanent linkages during vulcanization.

Rubber bushings were made based on Formulation 2 and Formulation 3 at hardness of 70 Shore A, and the static and dynamic properties were determined. Axial and radial compression tests showed that bushing based on Formulation 3 requires more force at high deflection, and give better rubber to metal bonding than Formulation 2. Dynamic test was carried out at radial direction for about 10 000 cycles. The results shows that bushing based on Formulation 3 gives higher isolation degree and lower transmissibility (lower transmission of vibration) compared to Formulation 2.

It can be concluded that a suitable formulation was successfully developed for bush mounting that gives an overall good balance in terms of mechanical properties, compression set, and ageing resistance with good isolation and transmissibility characteristics.

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDIES

In the study presented, rubber formulations for bush mounting (as shown in Figure 1.1) application by considering the mechanical and dynamic properties were developed. One of the major concerns of bush mounting is the dynamic application where it involves vibration isolation and dynamic stress. The damping causes the rubber part to develop heat internally. In an extreme case the part is destroyed by overheating and heat aging. To a greater or lesser degree this kind of stress also causes irreversible deformation, i.e., viscous flow of the rubber. The consequent fatigue suffered by the polymer network also causes crack formation and failure. A rubber part that is repeatedly elongated or flexed is exposed simultaneously to ozone. This, too, may lead to crack formation and destruction. Dynamic stressing of the interface or interfaces between rubber and a reinforcing material – metal, may destroy the adhesion, causing the part to fail (Rohde, 2001). In this project, natural rubber - polychloroprene rubber blends system were chosen to fulfill the above mentioned requirement.

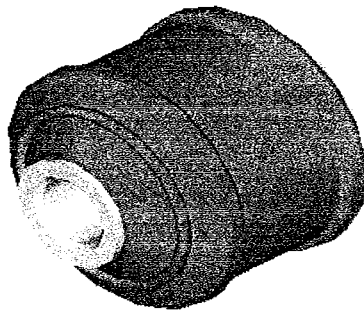


Figure 1.1: Rubber bushing

Natural rubber is a versatile and adaptable material which has been used successfully in engineering applications for 150 years, and remain the pre-eminent elastomer for springs and mountings. Natural rubber is a general purpose elastomer whose vulcanizates have a wide range of applications when suitably formulated. Natural rubber was chosen because it occupies a similar position with regard to rubber springs as spring steel does with metal springs (Lindley, 1984). Spring is one of the element of a vibratory system. The vibratory system can be idealized as a) mass, b) spring, c) damper and d) excitation as shown in Figure 1.2. The spring possesses elasticity, and under deformation, the work done is transformed into potential energy i.e. the strain energy stored in the spring. Vibration deals mainly with mechanical oscillatory motion of a dynamic system. Generally unwanted vibration in a machine may cause the loosening of parts and leads to failure. However, for vibrators, they are design to enhance vibration. Most frequently rubbery materials are used to control and mitigate the unwanted level of vibration and shock (Kamarul, 2000).

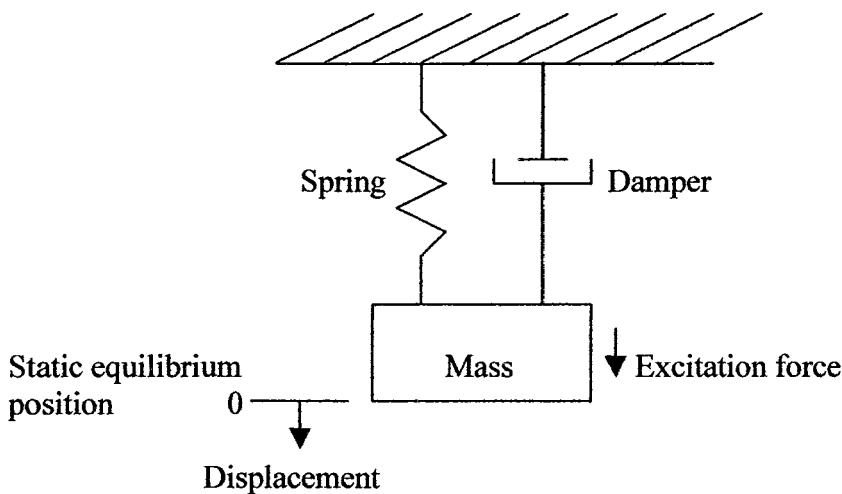


Figure 1.2: Elements of a vibratory system

Major areas of application which employ its outstanding physical properties are in vehicles, tyres, offshore and aerospace industries, civil engineering, and railways. The major advantage of natural rubber which makes it dominant in many dynamic applications, is its dynamic performance and the ability of rubber to carry a high load under compression, yet function at high strains and low stiffness compared to metals (Roberts, 1988). It has a low level of damping, and its properties remain fairly constant over the range 1 to 200 Hz, and show only slight increase to 1000Hz. Often, however, there are advantages in blending natural rubber with special elastomer because it enables one to confer special properties on the vulcanizates. A blend of chloroprene rubber in less than 40% is preferred due to consideration of good ozone, weathering, aging and oil resistance of the vulcanizates. It ought also to increase the degree of fire resistance (Matenar, 2001).

Natural rubber outstanding success as a spring rubber is due to the following characteristics:

- Excellent dynamic properties with low hysteresis loss.
- Excellent resistance to fatigue, cut growth and tearing.
- High resilience.
- Low heat build-up.
- Very efficient bonding to both metals and other reinforcing materials.
- Low cost and ease of manufacture.
- A wider range of operating temperature than most other rubbers.

Changes can occur in a rubber component as a result of the conditions under which it is stored or used. Most mechanical properties of rubbers are temperature dependent, but the changes are completely reversible provided that no chemical effects have occurred. Natural rubber is prone to degradation by oxygen at high temperatures; further vulcanization may also occur, resulting in increased hardness and decreased mechanical strength. The attack of oxygen proceed only slowly with natural rubber at normal atmospheric temperature, but the rate increases with temperature. In poorly protected vulcanizates, oxidation leads to increased long-term creep and stress relaxation, and to a general deterioration in mechanical properties. If unprotected natural rubber vulcanizates are subjected to tensile deformation, the concentration of ozone in the atmosphere at ground level (typically about 1 part per hundred million of air) is sufficient to cause surface cracking within a few weeks (Lindley, 1984).

Chloroprene rubber is a polar polymer with improved resistance to attack by non-polar oils and solvents. It has high toughness, good fire resistance, good weatherability and is easily bonded to metals. Polychloroprene is widely used for rubber goods subjected to dynamic stressing, for example; damping elements and spring components for motor vehicles and machinery, V-belts and timing belts, bellows, joint protection boots especially axle boots and conveyor belts (Rohde, 2001). Polychloroprene rubber with mercaptan modified general purpose grade has a medium rate of crystallization and Mooney viscosity $[ML(1+4)@100C = 45 - 53]$. It provides a good resistance to heat, oil and weather and it has an excellent storage stability. Mooney scorch and cure rate are quite stable during the storage of raw rubber. Its compounds band well and quickly on mixing mills, and fillers and oil can be

incorporated into it rapidly in an internal mixer (Musch, 2001). The structure of the polychloroprene is such that it is intrinsically highly resistant to ozone (Rohde, 2001).

Thus, blending of natural rubber with a suitable rubber such as chloroprene rubber at certain ratio is preferable to increase the resistance to environment and heat aging to achieve better static and dynamic properties of a bush mounting.

1.2 PROBLEM STATEMENT

According to Lindley (1973), the main requirement of most rubber engineering components is that their load-deformation behaviour should remain within the specified limits for a specified period of time. For mountings more relevant properties are stiffness, resilience, and resistance to creep. Other important parameters are fatigue resistance, low compression set and a minimal dependence of properties on strain amplitude, frequency of deformation and temperature. Many engineering components must be serviceable for over 30 years and therefore resistance to ageing is also a major consideration (Roberts, 1988). By considering the good dynamic properties for bush mounting (low compression set, lower natural frequency, high frequency ratio, high vibration isolation and lower transmissibility) a formulation with blend of natural rubber and chloroprene rubber will be studied. Natural rubber is the best rubber for superior dynamic properties except poor environmental resistance with respect to poor heat ageing resistance and is prone to degradation to oxygen and ozone attack. Pure natural rubber based rubber bushing can easily form cracks due to heat ageing, oxygen and ozone attack during the dynamic application. Polychloroprene rubber has a very good resistance to heat and ozone.

For dynamic application parts such as bush mounting, it is very important to have a good resistance to dynamic stressing as mentioned earlier. Provided that vulcanizates of equal hardness are compared, investigation of the relationship between compound formulation and resistance to dynamic stressing shows that the behaviour of the vulcanizates depends mainly on the crosslinking system (Rohde, 2001). Rhenogran ETU-80 is a special thiourea crosslinking system which is suitable for chloroprene rubber. The resistance to permanent deformation caused by static load or dynamic compressive stressing is an important criterion of the serviceability of such parts as bush mounting. Previous studies on chloroprene rubber shows that the compression set decreases as the Shore hardness rises and the reading are most favorable in the case of chloroprene rubber vulcanized with ETU (Rohde, 2001). For NR/CR blend, beside sulphur crosslinking system, the effect of addition of Rhenogran ETU-80 will be studied. It is expected to have a better crosslinking which contribute to lower compression set with the presence of Rhenogran ETU-80.

1.3 OBJECTIVES

The main aim of the research is to develop a suitable formulation, based on NR/CR blends, that has a good balance of mechanical properties, load-deflection and compression properties, and dynamic properties for a bush mounting application. Experimentally, the main objectives of the study are as follows:

- 1) To study the effect of blend ratio on the mechanical properties of NR/CR gum vulcanizates and filled vulcanizates.
- 2) To study the effect of carbon black loading on the vulcanizate properties of NR/CR blends.
- 3) To study the effect of special crosslinking system (ETU-80) on the cure characteristics, compression set and aging properties of NR/CR blend vulcanizates.
- 4) To study the effect of carbon black and processing oil on the mechanical and dynamic properties of NR/CR blends in the presence of ETU-80.
- 5) To study the load-deflection behaviour of NR/CR rubber vulcanizates at different hardness.
- 6) To study the axial and radial compression properties of NR/CR-based bush mounting.
- 7) To study the dynamic properties i.e. loss angle, dynamic stiffness, natural frequency, frequency ratio, vibration isolation and transmissibility of NR/CR-based bush mounting.

CHAPTER 2: LITERATURE REVIEW

2.1 LITERATURE REVIEW

The majority of rubber is used in the form of blends, an industrial fact of life, which is sufficient in itself to show the importance of vulcanization of blends. The aim of blending is to combine the desirable features of each component, but often the properties obtained are worse than anticipated from those of the component rubbers, and generally, the properties of vulcanized blends cannot be linearly interpolated from those of the individual rubber vulcanizates. Previous studies has been done on the rubbers and their ratio factors (Corish, 1994; Tinker & Jones, 1998; Livingstone & Longone, 1967), phase morphology (Hess *et al.*, 1993; Andrews, 1966; Roland, 1989) and the distribution of filler between the rubbers or at the interface (Herd & Bomo, 1995; Tsou & Waddell, 2002; Walters & Keyte, 1962; Mangaraj, 2002; Van de Ven & Noordermeer, 2000). The distribution of plasticizer (Aris *et al.*, 1995) and crosslinks (Tinker, 1995; Cook, 1999) between the rubbers and the interface: interpenetration of polymer chain segments, adhesion and crosslinking (Schuster *et al.*, 2000; Datta & Lohse, 1996) are special factors for blends.

2.1.1 Vulcanization of blends – crosslinking distribution and its effect on properties

Vulcanization is most commonly achieved by using a sulphur based cure system, and the complexities of this are well documented, if not completely understood yet. This complexity increases when rubber blends are vulcanized. This review is

focused on the crosslink distribution between rubber phases, which arise when blends of rubbers are vulcanized, how these distribution may be evaluated and controlled, and how they impact upon the properties of the blends (Chapman & Tinker, 2003). The blends are divided into three categories:

- 1) Rubbers differing primarily in polarity
- 2) Rubbers differing primarily in degree of unsaturation
- 3) Rubbers differing little in either polarity or degree of unsaturation

2.1.1 (a) Blends of rubbers differing mainly in polarity

The most extensively studied blends falling into this category are blends of NR with nitrile rubber, NBR, and there have been numerous reports of crosslink distribution for blends covering a range of acrylonitrile contents in NBR from 18% to 41% (Loadman & Tinker, 1989; Lewan, 1998; Brown *et al.*, 1993). Whilst NBR may appear to have a substantially lower level of unsaturation relative to NR, due to being a copolymer, in practice the higher density of NBR and lower molecular weight of the butadiene repeat unit lead to a molar concentration of unsaturation of about 11×10^3 mol/m³ for high acrylonitrile NBR in comparison with about 13×10^3 mol/ m³ for NR. The primary influence on crosslink distribution is therefore the difference in polarity of the two elastomers and its effect on distribution of curatives and vulcanization intermediates.

Sulphur will always distribute in favour of the NBR phase due to its high solubility parameter (29.8 MPa^{1/2}). The solubility parameter of NR is 16.7 MPa^{1/2}, whilst those for NBR lie between 17.8 MPa^{1/2} and 21.3 MPa^{1/2}. Control of crosslink distribution will therefore depend largely on how the accelerator(s), and vulcanization intermediates, partition between the rubbers (Chapman & Tinker, 2003).

An extreme example is provided by NBRs with acrylonitrile contents of 18% and 41% (NBR 18 and NBR 41 respectively) cured with cure systems containing related accelerators differing greatly in polarity – TMTD and N, N'-diisopropylthiuram disulphide (ODIP) (Lewan, 1998). Crosslinking densities as determined by swollen-state NMR spectroscopy are presented in Figure 2.1. It should be noted that the two thiuram accelerators were used at equimolar levels. The data in Table 2.1 show a decrease in efficiency of vulcanization in the NBR phase of NR/NBR 18 blends and an increase in efficiency in the NR phase of NR/NBR 41 blends when ODIP is substituted for TMTD.

The impact of both choice of accelerator and acrylonitrile content of the NBR is immediately apparent. The highly polar TMTD is clearly a poor choice of accelerator for NR/NBR blends-the extreme imbalance of crosslinks in favour of the NBR phase may be attributed to partition of both sulphur and TMTD in favour of NBR. When TMTD is replaced by the less polar ODIP, the imbalance in crosslink distribution is reduced in NR/NBR 18 blends through a doubling of crosslink density in the NR phase. This may be attributed to an increase in concentration of accelerator in the NR phase. A greater increase in NR crosslink density is seen in NR/NBR 41 blends, and this is accompanied by a dramatic decrease in crosslinking of the NBR phase; there is a substantial reduction in overall crosslink density. This may be explained by the NBR phase containing the majority of the sulphur due to a favourable partition coefficient, but the NR phase containing most of the accelerator. The large phase sizes in this blend ($> 20\mu\text{m}$) preclude diffusion of vulcanization intermediates playing a significant role in determining crosslink distribution.

This explanation receives support from a consideration of the type of crosslinks present in each phase, as determined by a combination of chemical probe treatment thiol-amines (Saville & Watson, 1967; Campbell, 1969) and swollen- state NMR spectroscopy (Lewan, 1998)

2.1.1 (b) Blends of rubbers differing primarily in degree of unsaturation

The classic example of this type of blend is NR with EPDM, and the great commercial potential of this system has resulted in numerous attempts (Mueller & Frueh, 2000; Ghosh & Basu, 2002) to overcome the inherent difficulties associated

Crosslink density, mol/m³

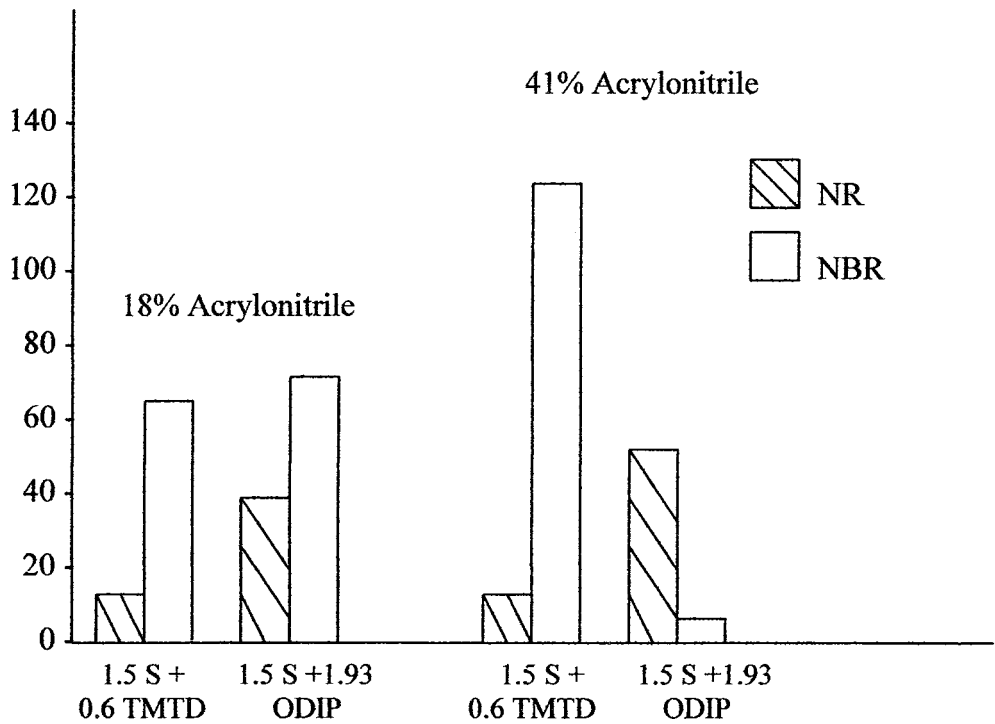


Figure 2.1: Crosslinking densities (Chapman & Tinker, 2003)

Table 2.1: Percentage of each type of sulphidic in the NR and NBR phases of 50:50

NR:NBR blends cured with 1.5phr sulphur and either 0.6phr TMTD or 1.93phr ODIP (Chapman & Tinker, 2003)

Crosslink	NBR 18				NBR 41			
	TMTD		ODIP		TMTD		ODIP	
	NBR	NR	NBR	NR	NBR	NR	NBR	NR
Poly-	14	100	39	100	24	100	26	22
Di-	41	-	22	-	26	-	-	78
Mono-	45	-	39	-	30	-	74	-

with vulcanizing two elastomers differing so much in unsaturation. It should also be recognized that there will be a tendency for curatives and vulcanization intermediates to partition in favour of the NR phase (Hess *et al.*, 1993); indeed the use of dithiophosphate accelerators, which have high solubility in both NR and EPDM, has been found to lead to improved blend properties (Mueller & Frueh, 2000; Ghosh & Basu, 2002).

Success in increasing crosslinking in the EPDM phase was generally inferred from an improvement in physical properties, particularly modulus and tensile strength as illustrated in Table 2.2 and 2.3, which summarize results obtained by (Hopper, 1976) when modifying EPDM with N-chlorothioamides and (Coran, 1988) when modifying maleic anhydride. Although the two approaches are different, the former aiming to enforce sulphur vulcanization in the EPDM by attaching a pendent prevulcanization inhibitor and the later aiming to introduce a second, ionomeric network in the EPDM, the net result is similar.

Table 2.2: Effect of modification of EPDM with N-chlorothioamide on physical properties of 70:30 IR/EPDM blend ** (Hopper, 1976)

Property	Unmodified EPDM	Modified EPDM*
Rheometer torque, Nm	6.52	7.73
M300, MPa	12.9	14.3
Tensile strength, MPa	17.7	22.8
Elongation at break, %	400	450

** Blends of Natsyn 200 with Nordel 1470 containing 50 phr FEF black, 4phr ZnO, 1.5phr stearic acid, 1phr phenolic antioxidant, 2phr sulphur, 1phr MBS
 * Modified with 0.14mol/kg N-chlorothio-N-methyl-p-toluenesulphonamide.

Table 2.3: Effect of modification of EPDM with maleic anhydride on physical properties of 70:30 NR/EPDM blend ** (Coran, 1988)

Property	Unmodified EPDM	Modified EPDM*
M300, MPa	7.7	8.0
Tensile strength, MPa	14.8	23.3
Elongation at break, %	500	602
Fatigue life:		
0 – 100% Strain, kcs	26	46
0 – 10 kg/cm ² Energy, kcs	18	41

** Blends of SMR5 with Epsyn 70-A containing 50phr N326 black, 10phr oil, 5.5phr ZnO, 2phr stearic acid, 2phr sulphur, 0.5phr TBBS.
 * Modified with 2% maleic anhydride.

Similar levels of crosslinking may be attained in NR/EPDM blends if the EPDM has very high ENB level (Wirth, 1970) and also of very high molecular weight (Rooney *et al.*, 1994), as shown in Table 2.4. The effect of both ENB level and molecular weight is confirmed by a swollen-state NMR study which did not go to the length of calibrating peak width against crosslink density (Van Duin *et al.*, 1993).

Table 2.4: Crosslink densities in 60:40 NR: EPDM** blends cured to optimum (t95+5) and overcured at 166⁰C (2phr sulphur, 0.5phr MBS) (Rooney *et al.*, 1994)

Cure time, min	12	30
NR <i>n</i> phys, mol/m ³	61	47
EPDM <i>n</i> phys, mol/m ³	25.5	25

** Polysar experimental polymer: 10.5wt%ENB,
Mooney viscosity ML(1+4) at 150⁰C = 70.

The use of a hybrid accelerated sulphur/peroxide cure has also been advocated (Brodsky, 1994; Ferrandino & Hong, 1997). Although some partitioning of the peroxide is to be expected, any peroxide in the EPDM phase will result in crosslinking of the EPDM. Only low levels of peroxide will be necessary to induce the moderate crosslink density known to be needed for good properties, and 0.6phr dicumyl peroxide has been found to give improvements in cut growth and dynamic ozone resistance. This approach has parallels with that of (Coran, 1988), in that the crosslinks formed in the EPDM may be expected to be predominantly not sulphidic in nature. Recent studies have indicated that satisfactory blend properties can be achieved if an EPDM with high ethylene content is used (Pechenova *et.al.*, 2001); the importance of filler distribution was also stressed.

2.1.1 (c) Blends differing little in polarity or unsaturation

These blends are exemplified by blends of the general purpose rubbers – NR, BR and SBR. Of these, blends of NR or IR and BR have received most attention. At first sight, these elastomers would appear to differ so little that it might be anticipated that an even distribution of crosslinks would be norm. In practice, there are significant differences, and not those which may be inferred from a simple comparison of the rheometer cure behaviour of comparable compounds of the two; this shows the NR to cure much quicker, but the naturally occurring cure activators and accelerators might be expected to partition fairly evenly between the two rubbers once they are blended, and so NR would lose this advantage.

A deeper consideration of the rubber and the literature points to BR being likely to crosslink preferentially in a blend with NR. Both sulphur and the common sulphenamide accelerators will partition slightly in favour of the BR (Freitas *et al.*, 2003). Moreover, it has been argued that the unsaturation in BR may be more reactive towards sulphur vulcanization (Butring *et al.*, 1997). The concentration of double bonds is also greater for BR, about 17 mol/dm³ versus about 13 mol/dm³ for NR.

The first reports of crosslink density distribution for NR/BR blends cured with sulphur / sulphenamide or sulphur / TMTD were in accord with this prediction: the BR was the more highly cured phase (Brown & Tinker, 1993). Subsequently, a study of IR/BR blends through the cure by swollen-state NMR spectroscopy indicated that, whilst the BR phase was the more highly crosslinked at optimum cure, crosslinks formed preferentially in the IR phase in the early stages of vulcanization (Shershnev *et*

al., 1993). However, a later report of the vulcanization of NR/BR blends with conventional and semi-EV cure systems based on the three most common sulphenamide accelerators indicated that the BR phase begins to cure before the NR phase at 150 °C, and that the latter tends not to catch up.

The question remains as to whether changing the crosslink distribution will improve the properties of NR/BR blends. Figure 2.2 shows how the crosslink density distribution in a 70:30 black-filled vulcanizate can be adjusted by modification of one of the phases prior to crossblending. This altered crosslink distribution led to improved passenger tyre wear performance, as shown in Figure 2.3. In a very recent study of unfilled NR/BR blends (Butring *et al.*, 1997), crosslink density distributions were not determined, but it was found that promotion of crosslinking in the NR phase (by incorporating the sulphur, zinc oxide and stearic acid in the NR before crossblending) led to reduced tensile strength and elongation at break. However, all of the reported tensile strengths (of both the blends and the individual rubbers) were much lower than normally expected for these rubbers.

S/CBS equivalent, phr

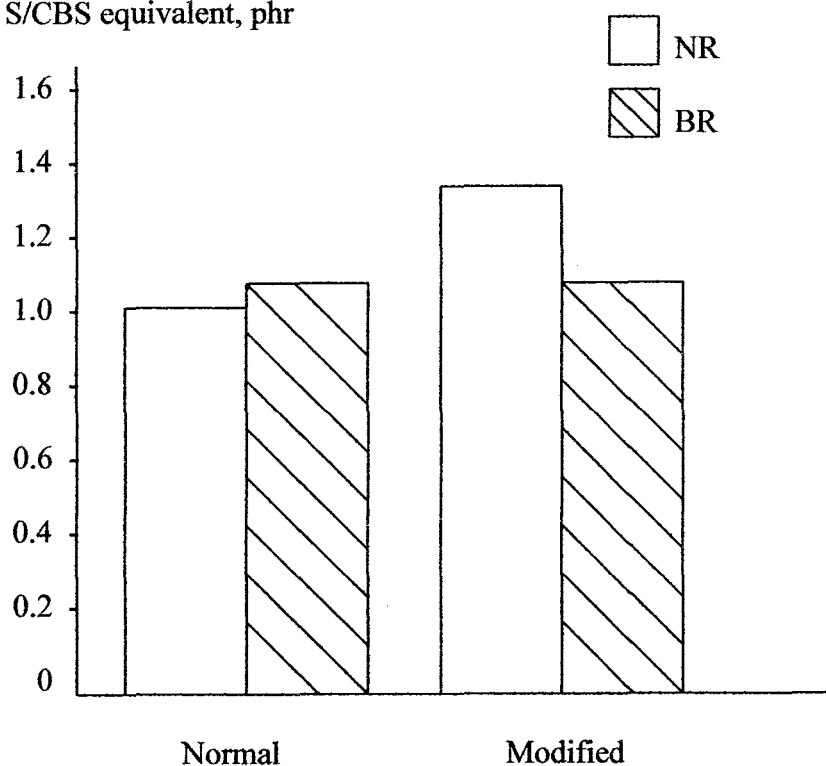


Figure 2.2: Crosslink density distribution (Groves, 1998)

Wear rating

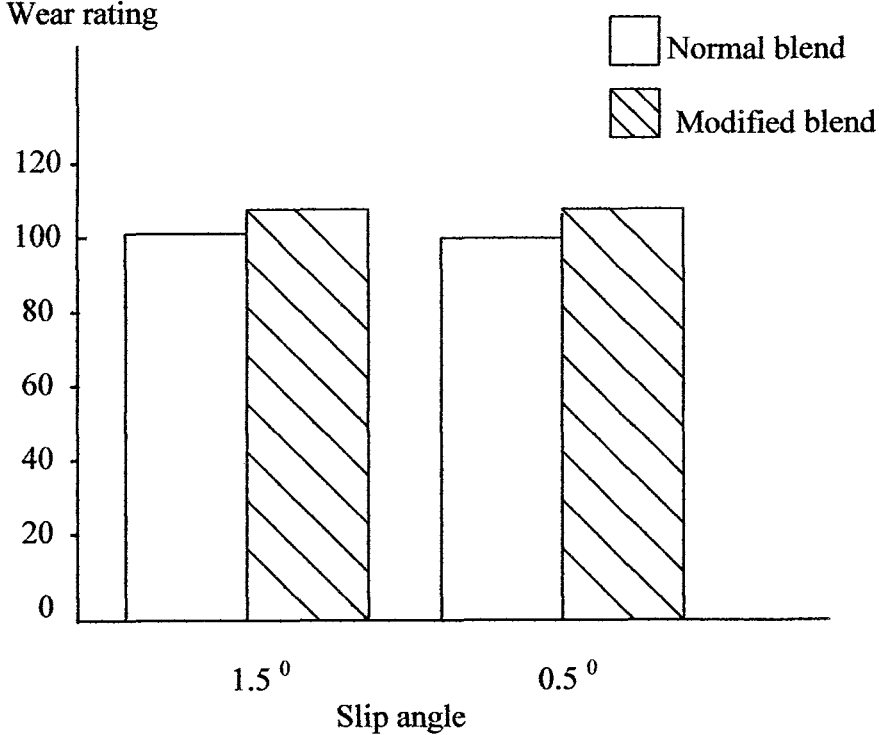


Figure 2.3: Passenger tyre wear performance (Chapman & Tinker, 2003)

Even blends which are not considered to be problematic and which appear to differ little in either polarity or degree of unsaturation, such as NR/BR blends, have been shown to suffer uneven crosslink distribution in sulphur vulcanization. Improvements in properties have been achieved by manipulating the crosslink distribution.

Control of crosslink distribution is important if the best is to be obtained from vulcanized blends. Application of the principles described here has provided improvements in physical properties and allowed successful use blends which have problematic in the past.

2.1.2 Curing characteristics and mechanical properties of natural rubber / chloroprene rubber and epoxidized natural rubber / chloroprene rubber blends

Polymer blends are being used extensively in numerous applications. A blend can offer a set of properties that may give it the potential of entering application areas not possible with either of the polymers comprising the blend. Chloroprene rubbers are homopolymers of chloroprene. The polymer chains have an almost entirely *trans*-1,4-configuration. Because of this high degree of stereoregularity they are able to crystallize on stretching. Consequently, the gum vulcanizates have high tensile strength and resemble natural rubber gum vulcanizates (Nagdi, 1993). Epoxidized natural rubber is a modified natural rubber having properties resembling those of synthetic rubbers rather than natural rubber (Davis *et al.*, 1983; Baker & Gelling, 1985). ENR has unique properties such as good oil resistance, low gas permeability, improved wet grip and

rolling resistance, coupled with high strength. Many blends based on ENR and other polymers, like SBR (Nasir & Choo, 1989; Ismail & Suzaimah, 2000), NR (Poh & Khok, 2000), BR (Baker *et al.*, 1985) and PVC (Ishiaku *et al.*, 1999) have been reported.

A typical formulation used for this study is shown in Table 2.5. Cure assessment was carried out using a Mooney Viscometer MV 2000 at three different temperatures, 120 °C, 130 °C and 140 °C (Ismail & Leong, 2000). The MV 2000 gives digital outputs of curing characteristics such as t5 (time required to achieve 5 Mooney units above the minimum viscosity), t35 (time required to achieve 35 Mooney units above the minimum viscosity) and minimum Mooney viscosity.

Table 2.5: The formulation used in the preparation of a rubber blend compound (Ismail & Leong, 2000)

	phr
Rubber blend	100
Stearic acid	1.0
Zinc oxide	5.0
Magnesium oxide	2.0
CBS	1.0
ETU	0.5
Sulphur	2.5

The Mooney scorch time, t_5 with blend ratio for SMR L/CR and ENR 50/CR blends at three different temperatures: 120 °C, 130 °C and 140 °C exhibits negative deviation of the scorch time of the blend from calculated value based on the interpolation between the scorch time of the two components elastomers. The scorch time, t_5 of CR is longer than SMR L and ENR 50 and this is a cure characteristic of CR, that is, the prevention of scorch (Vanderbilt, 1990). At 130 °C, the t_5 for both blends shows that the t_5 of ENR 50 is shorter than SMR L followed by CR. Owing to the activation of an adjacent double bond by the epoxide group, the t_5 for ENR 50 is shorter than that of SMR L (Poh & Tan, 1991). The negative deviation of scorch time from the interpolated value is attributed to the induction effect of ENR 50 and SMR L on CR molecules that causes an overall increase in the rate of crosslinking of the blend. The induction effect of ENR 50 is higher than SMR L. Probably more activated precursors to crosslink are formed as a result of the activation of the double bond by the epoxide group (Coran, 1964).

Lower viscosity of SMR L and ENR 50 compared to CR causes reduced cure index with increasing composition of SMR L and ENR 50. In blends, the lower viscosity components tend to form a continuous phase (Miles & Zurek, 1998; Lee *et al.*, 1991), which more or less governs the curing process. However, at similar blend ratio ENR/CR blend exhibits lower curing index than SMR L/CR blend.

For both SMR L/CR and ENR 50/CR blends, a positive deviation of tensile modulus and hardness from the ideal is observed, suggesting that synergism has occurred and the maximum value of tensile modulus and hardness is obtained at 25% of SMR L or ENR 50. All CR, SMR L and ENR 50 undergo strain-induced

crystallization; the rubbers reinforced each other when subjected to tensile stress, as reflected by a higher tensile modulus obtained in the blend. However, for tensile strength of the blends, the positive deviation occurred at 75% of SMR L or ENR 50 suggesting that the best blend ratio is 75/25 (wt/wt) of ENR 50/CR or SMR L/CR to obtain good tensile strength of the blend (Ismail & Leong, 2001).

2.1.3 Studies on the cure and mechanical properties of blends of natural rubber with dichlorocarbene modified styrene-butadiene (DCSBR) and chloroprene rubber

Elastomer blends are frequently used in the rubber industry to obtain best compromise in compound physical properties, processability and cost. A blend can offer a set of properties that can give it the potential of entering application area not possible with either of the polymer comprising the blend. It has been already reported that the blending of natural rubber with other elastomers can improve its properties to great extent. For example, blends of NR with Styrene butadiene rubber (SBR) are noted for a combination of properties such as good abrasion resistance (Joseph *et al.*, 1988), while those with nitrile rubber (NBR) are noted for its excellent oil resistance (Choi, 2002), those with chloroprene rubber (CR) are noted for good weather resistance (El-Sabbagh, 2003). Several studies in the area of NR/EPDM are available in the literature with special reference to different blend ratio of NR:EPDM, which can improve excellent ozone resistance (Schulz *et al.*, 1982).

NR suffers from poor flame, weather, ozone, oil and thermal properties. Due to the strain induced crystallization behavior of NR, which can increase the modulus, resistance to deformation and stabilize the system by preventing the propagation of the defects without the use of highly reinforcing fillers and expensive coupling agents. DCSBR can also provide strain induced crystallization behavior with lower compression set, flame and oil resistance (Ramesan & Alex, 2000). CR is a homopolymer with trans 1,4 configuration and it is able to crystallize on stretching so the gum vulcanizate have good tensile strength (Gent, 1965). The present paper reports the comparison of cure characteristics and mechanical properties of 70/30, 50/50, 30/70 compositions of NR/DCSBR and NR/CR blends. The effect of temperature on the cure characteristics of the blends is also evaluated. Oil swelling behavior of the vulcanizate is analyzed giving emphasis to the influence of temperature. The recipe used is shown in Table 2.6 (Ramesan *et al.*, 2004).

Table 2.6: Basic formulation used for NR/DCSBR and NR/CR blends (Ramesan et.al, 2004)

Ingredients	phr
Rubber blends ^a	100
Stearic acid	2.0
Zinc oxide	5.0
Antioxidant TDQ ^b	1.0
Magnesium oxide	2.0
CBS ^c	1.0
TMTD ^d	0.5
ETU ^e	0.5
Sulphur	2.2

^a NR/DCSBR and NR/CR were used with blend ratio of 100/0, 70/30, 50/50, 30/70, 0/100.

^b 2,2,4-Trimethyl-1,2-dihydroquinoline.

^c N-Cyclohexyl-2-benzothiazyl sulphenamide.

^d Tetramethylthiuram disulphide.

^e Ethylene thiourea

2.1.3 (a) Cure characteristics

In NR/DCSBR blend, there is a decrease in cure index with increasing the composition of NR might be due to the lower viscosity of NR compared to DCSBR and CR. The lower viscosity components lead to form a continuous phase in blends